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(54) [TITLE OF THE INVENTION] Organic EL element

(57) [ABSTRACT]

[Object] To provide a long-life organic EL element with which deterioration of light emission characteristics by oxygen or moisture is prevented and stable light emission characteristics are maintained over a long period.

[Structural unit] A protective layer 3 and, on the outer side of this, a sealing layer 4 consisting of an oxygen absorption layer 41 and an oxygen barrier layer 42 are deposited to constitute a laminate 2 on the outer side of a structural unit 1 consisting of an anode 12, organic light-emitting material 14 and a cathode 13.

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Key to drawing text sheet 1

- 1: Structural unit
- 2: Laminate
- 3: Protective layer
- 4: Sealing layer
- 5: Frame
- 10: Organic EL element
- 11: Substrate
- 12: Anode
- 13: Cathode
- 14: Organic light-emitting material
- 41: Oxygen barrier layer
- 42: Oxygen absorption layer

[WHAT IS CLAIMED IS]

[Claim 1] In an organic EL element possessing a structural unit in which organic light-emitting material is gripped between a pair of mutually facing electrodes, at least one of which is transparent or semi-transparent, and a laminate which consists of a protective layer and/or a sealing layer and is provided on the outer side of said structural unit,

an organic EL element in which said laminate's sealing layer is a layer comprising one or more sets of double layers consisting of an oxygen barrier layer and an oxygen absorption layer.

[Claim 2] Organic EL element as claimed in Claim 1, wherein said set of double layers consisting of oxygen barrier layer and oxygen absorption layer is constituted by depositing an oxygen absorption layer and an oxygen barrier layer, in that order, on the electrode side which is the cathode side within said a pair of mutually facing electrodes.

[Claim 3] Organic EL element as claimed in Claim 1, wherein said structural unit possesses a substrate, an anode, a positive hole injection-transport layer, a light-emitting layer, an electron injection-transport layer, a cathode, a protective layer and a sealing layer in that order, and wherein said sealing layer is a layer possessing at least one set of double layers comprising an oxygen absorption layer and an oxygen barrier layer in that order.

[Claim 4] In an organic EL element possessing a structural unit in which organic light-emitting material is gripped between a pair of mutually facing electrodes, at least one of which is transparent or semi-transparent, and a laminate which consists of a protective layer and/or a sealing layer and is provided on the outer side of said structural unit,

an organic EL element in which at least one out of said laminate's protective layer and sealing layer contains material which adsorbs, occludes or consumes oxygen.

[Claim 5] Organic EL element as claimed in any one of Claims 1-3, wherein said laminate's protective layer contains material which adsorbs, occludes or consumes oxygen.

[Claim 6] Organic EL element as claimed in Claim 4 or 5, wherein said material which adsorbs, occludes or consumes oxygen is constituted by one or more substances selected from the group consisting of magnesium oxide, magnesium carbonate, iron oxide, titanium oxide, bentonite, acidic clay, montmorillonite, kieselguhr (clay mineral), activated alumina, silica-alumina, zeolite, silica, zirconia and activated carbon.

[Claim 7] Organic EL element as claimed in Claim 4 or 5, wherein said material which adsorbs, occludes or consumes oxygen is constituted by a fine powder or thin film of a metal of the 4th period of the periodic table or a salt or an oxide of said metal or by material in which a fine powder or thin film of a metal of the 4th period of the periodic table or a salt or an oxide of said metal is carried at a concentration of $\leq 10\%$ by weight on one or more substances selected from the group consisting of magnesium oxide, magnesium carbonate, iron oxide, titanium oxide, bentonite, acidic clay, montmorillonite, kieselguhr (clay mineral), activated alumina, silica-alumina, zeolite, silica, zirconia and activated carbon.

[Claim 8] Organic EL element as claimed in Claim 7, wherein said metal of the 4th period of the periodic table is constituted by Co, Ni, Mn, Cr, V, Zn or Cu alone or an alloy of one or more of these substances.

[Claim 9] Organic EL element as claimed in Claim 8, wherein the alloy of said metal of the 4th period of the periodic table is cobalt oxide (II).

[Claim 10] Organic EL element as claimed in Claim 4 or 5, wherein said material which adsorbs, occludes or consumes oxygen is constituted by material in which a primary or secondary carbon-possessing hydrocarbon with 3-30 carbon atoms is impregnated at a concentration of $\leq 1\%$ by weight in

activated carbon, or in a fine powder or thin film of a metal of the 4th period of the periodic table or a salt or an oxide of said metal, or in material in which a fine powder or thin film of a metal of the 4th period of the periodic table or a salt or an oxide of said metal is carried at a concentration of $\leq 10\%$ by weight on one or more substances selected from the group consisting of magnesium oxide, magnesium carbonate, iron oxide, titanium oxide, bentonite, acidic clay, montmorillonite, kieselguhr (clay mineral), activated alumina, silica-alumina, zeolite, silica, zirconia and activated carbon.

[Claim 11] Organic EL element as claimed in Claim 4 or 5, wherein said material which adsorbs, occludes or consumes oxygen is constituted by material in which platinum, palladium, rhodium, ruthenium or silver is carried at a concentration of $\leq 5\%$ by weight by one or more substances selected from the group consisting of magnesium oxide, magnesium carbonate, iron oxide, titanium oxide, bentonite, acidic clay, montmorillonite, kieselguhr (clay mineral), activated alumina, silica-alumina, zeolite, silica, zirconia and activated carbon.

[Claim 12] In an organic EL element possessing a structural unit in which organic light-emitting material is gripped between a pair of mutually facing electrodes, at least one of which is transparent or semi-transparent, and a laminate which consists of a protective layer and/or a sealing layer and is provided on the outer side of said structural unit,

an organic EL element in which said laminate's protective layer contains a dehydrating agent.

[Claim 13] Organic EL element as claimed in any one of Claims 1-11, wherein said laminate's protective layer contains a dehydrating agent.

[Claim 14] Organic EL element as claimed in 12 or 13, wherein said laminate's protective layer is constituted by a solid organic substance.

[Claim 15] Organic EL element as claimed in any one of Claims 12-14, wherein said dehydrating agent is constituted by an alkali metal or an alkaline earth metal.

[Claim 16] In an organic EL element possessing a structural unit in which organic light-emitting material is gripped between a pair of mutually facing electrodes, at least one of which is transparent or semi-transparent, and a laminate which consists of a protective layer and/or a sealing layer and is provided on the outer side of said structural unit, an organic EL element in which said laminate's sealing layer is constituted by a photo-or thermosetting resin containing an inorganic composition.

[Claim 17] Organic EL element as claimed in any one of Claims 1-15, wherein said laminate's sealing layer is constituted by a photo-or thermosetting curable resin containing an inorganic composition.

[Claim 18] Organic EL element as claimed in Claim 16 or 17, wherein said inorganic composition is silica glass.

[Claim 19] In an organic EL element possessing a structural unit in which organic light-emitting material is gripped between a pair of mutually facing electrodes, at least one of which is transparent or semi-transparent, and a laminate which consists of a protective layer and/or a sealing layer and is provided on the outer side of said structural unit, an organic EL element in which at least one out of said laminate's protective layer and sealing layer comprises at least one organic layer whose oxygen permeability coefficient is $\leq 1 \times 10^{-12}$ cc.cm/cm².S (cmHg).

[Claim 20] Organic EL element as claimed in any one of Claims 1-11, wherein said laminate's protective layer comprises at least one organic layer whose oxygen permeability coefficient is $\leq 1 \times 10^{-12}$ cc.cm/cm².S (cmHg).

[Claim 21] Organic EL element as claimed in any one of Claims 1-11, wherein said laminate's sealing layer comprises at least

ne organic layer whose oxygen permeability coefficient is $\leq 1 \times 10^{-12}$ cc.cm/cm².S (cmHg).

[Claim 22] Organic EL element as claimed in any one of claims 1-18, which further comprises, at the outer side of said laminate's sealing layer, at least one organic layer whose oxygen permeability coefficient is $\leq 1 \times 10^{-12}$ cc.cm/cm².S (cmHg).

[DETAILED DESCRIPTION OF THE INVENTION]

[0001]

[Field of industrial use] The present invention relates to an organic EL (electroluminescent) element. More particularly, the invention relates to a long-life organic EL element which can be suitably employed in various types of displays and light-emitting elements for information industry equipment and which maintains stable light emission characteristics over a long period.

[0002]

[Prior art] An organic EL element is constituted by a structural unit in which organic light-emitting material is sandwiched between a pair of facing electrodes, and is an element in which electrons are injected from one electrode, positive holes are injected from the other electrode. Emission of light is brought about when the injected electrons and positive holes recombine in the light-emitting layer. Work is going forward on the development of organic EL elements, since they have good impact resistance and viewability and they offer promise for use as alternatives to LEDs and, given the variety of colours emitted by organic substances, for use in full-colour flat panel displays.

[0003] It is known that, when these organic EL elements are driven continuously or intermittently over a set period, the light emission characteristics such as the brightness of the emitted light, the luminous efficiency and the uniformity of the emitted light, etc. deteriorate considerably compared to the characteristics in the initial period. Causes one can cite for this deterioration of the light emission characteristics include oxidation of electrodes by oxygen

which penetrates into the interior of the organic EL elements, and deterioration of organic substances caused by infiltration of the moisture of air into the organic EL elements. Other causes which can be cited include the facts that peeling and structure interfaces occurs due to the effects of oxygen and moisture, and, triggered by the production of heat when the elements are driven and the high-temperature environment during element drive, etc., stress due to the differences between the coefficients of thermal expansion of constituent parts of the structures is produced at structure interfaces, so resulting in interface peeling and other forms of mechanical deterioration of the structure.

[0004] By way of inventions which prevent this deterioration of light emission characteristics, there have been disclosed (1) a sealing method in which a protective film constituted by an electrically insulating inorganic compound is provided on the outer surface of the laminate structural unit of an organic EL element, and a shield layer of a substance selected from the group consisting of electrically insulating gastight fluids and electrically insulating high polymer compounds such as electrically insulating glass, epoxy resin and silicone resin, etc. is provided on the outer side of this protective layer (disclosure of Japanese Laid-open Patent Application Hei No. 5-89959), (2) a thin-film EL panel in which thin-film EL elements are sealed by a back-surface substrate and insulating material in the form of a solid or a gel which contains a moisture absorbent (disclosure of Japanese Laid-open Patent Application Hei No. 2-12792), (3) a method in which EL elements are packed in a case, and phosphorus pentoxide too is caused to be present in the case in a manner in which it does not contact the EL elements (disclosure of Japanese Laid-open Patent Application Hei No. 3-261091), (4) methods for removing moisture by immersing an EL element in a fluorocarbon oil and admixing a dehydrating agent in this fluorocarbon oil (disclosure of Japanese Laid-open Patent Application Hei Nos. 5-41281 and 114486) and (5) a technique for gastight and highly humidity-resistant sealing using a phot setting resin (disclosure of Japanese Laid-open Patent Application Hei No. 5-182759), etc.

[0005]

[Problems intended to be resolved by the invention] However, with the sealing method of (1) noted above, the sealing effect in respect of oxygen is not always fully satisfactory, with the thin-film EL panel of (2), again, the sealing effect in respect of oxygen is unsatisfactory, with the method of (3), element manufacture is complex and troublesome, since EL elements are packed in a case in which it is necessary to produce a separate container containing phosphorus pentoxide, in addition to which the method is not practical since phosphorus pentoxide reacts violently with the electrodes and organic materials of EL elements and it is therefore necessary to take care over the impact resistance, with the method of (4), since fluorocarbon oil is liquid, handling at the time of sealing is difficult, in addition to which the method is not practical, since there is a risk of liquid leakage if breakage occurs, and with the method of (5), there is the problem that the element deteriorates mechanically, leading to breakage due to shrinkage at the time of curing of the resin which is used and to the difference between the expansion of the EL element and that of the sealing layer (due to temperature cycles). The present invention has been devised in view of the above problems, and it has as its object to provide a long-life light-reflecting element with which deterioration of light emission characteristics due to oxygen or moisture is prevented and stable light emission characteristics are maintained over a long period. Another object of the invention is to provide a long-life organic EL element with which mechanical deterioration due to temperature cycles is prevented and stable light emission characteristics are maintained over a long periods.

[0006]

[Means for resolving the problems] In order to achieve the above objects, according to the invention there is provided an organic EL element in which, in an organic EL element an organic EL element possessing a structural unit in which organic light-emitting material is gripped between a pair of mutually facing electrodes, at least one of which is transparent or semi-transparent, and a laminate which consists of a protective layer and/or a sealing layer and is provided

on the outer side of the structural unit, the laminate's sealing layer is a layer comprising one or more sets of double layers consisting of an oxygen barrier layer and an oxygen absorption layer.

[0007] There is further provided an organic EL element in which the set of double layers consisting of an oxygen barrier layer and an oxygen absorption layer is constituted by depositing an oxygen absorption layer and an oxygen barrier layer, in that order, on the electrode side which is the cathode side within the a pair of mutually facing electrodes.

[0008] There is further provided an organic EL element in which the structural unit possesses a substrate, an anode, a positive hole injection-transport layer, a light-emitting layer, an electron injection-transport layer, a cathode, a protective layer and a sealing layer in that order, and whose sealing layer is a layer possessing at least one set of double layers comprising an oxygen absorption layer and an oxygen barrier layer in that order.

[0009] There is further provided an organic EL element in which, in an organic EL element possessing a structural unit in which organic light-emitting material is gripped between a pair of mutually facing electrodes, at least one of which is transparent or semi-transparent, and a laminate which consists of a protective layer and/or a sealing layer and is provided on the outer side of the structural unit, at least one out of the laminate's protective layer and sealing layer contains material which adsorbs, occludes or consumes oxygen.

[0010] There is further provided an organic EL element in which the laminate's protective layer contains material which adsorbs, occludes or consumes oxygen.

[0011] There is further provided an organic EL element in which the material which adsorbs, occludes or consumes oxygen is constituted by one or more substances selected from the group consisting of magnesium oxide, magnesium carbonate, iron oxide, titanium oxide, bentonite, acidic clay,

montmorillonite, kieselguhr (clay mineral), activated alumina, silica-alumina, zeolite, silica, zirconia and activated carbon.

[0012] There is further provided an organic EL element in which the material which adsorbs, occludes or consumes oxygen is constituted by a fine powder or thin film of a metal of the 4th period of the periodic table or a salt or an oxide of this metal or by material in which a fine powder or thin film of a metal of the 4th period of the periodic table or a salt or an oxide of this metal is carried at a concentration of ≤ 10 wt% on one or more substances selected from the group consisting of magnesium oxide, magnesium carbonate, iron oxide, titanium oxide, bentonite, acidic clay,

montmorillonite, kieselguhr (clay mineral), activated alumina, silica-alumina, zeolite, silica, zirconia and activated carbon.

[0013] There is further provided an organic EL element in which the metal of the 4th period of the periodic table is constituted by Co, Ni, Mn, Cr, V, Zn or Cu alone or an alloy of one or more of these substances.

[0014] There is further provided an organic EL element in which the alloy of the metal of the 4th period of the periodic table is cobalt oxide (II).

[0015] There is further provided an organic EL element in which the material which adsorbs, occludes or consumes oxygen is constituted by material in which a primary or secondary carbon-possessing hydrocarbon with 3-30 carbon atoms is impregnated at a concentration of ≤ 1 wt% in activated carbon, or in a fine powder or thin film of a metal of the 4th period of the periodic table or a salt or an oxide of this metal, or in material in which a fine powder or thin film of a metal of the 4th period of the periodic table or a salt or an oxide of this metal is carried at a concentration of ≤ 10 wt% on one or more substances selected from the group consisting of magnesium oxide, magnesium carbonate, iron oxide, titanium oxide, bentonite, acidic clay, montmorillonite, kieselguhr

(clay mineral), activated alumina, silica-alumina, zeolite, silica, zirconia and activated carbon.

[0016] There is further provided an organic EL element in which the material which adsorbs, occludes or consumes oxygen is material in which platinum, palladium, rhodium, ruthenium or silver is carried at a concentration of ≤ 5 wt% by one or more substances selected from the group consisting of magnesium oxide, magnesium carbonate, iron oxide, titanium oxide, bentonite, acidic clay, montmorillonite, kieselguhr (clay mineral), activated alumina, silica-alumina, zeolite, silica, zirconia and activated carbon.

[0017] There is further provided an organic EL element in which, in an organic EL element possessing a structural unit in which organic light-emitting material is gripped between a pair of mutually facing electrodes, at least one of which is transparent or semi-transparent, and a laminate which consists of a protective layer and/or a sealing layer and is provided on the outer side of the structural unit, the laminate's protective layer contains a dehydrating agent.

[0018] There is further provided an organic EL element in which the laminate's protective layer contains a dehydrating agent. Tr. note: Repetition as in text.)

[0019] There is further provided an organic EL element in which the laminate's protective layer is constituted by a solid organic substance.

[0020] There is further provided an organic EL element in which the abovenoted dehydrating agent is constituted by an alkali metal or an alkaline earth metal.

[0021] There is further provided an organic EL element in which, in an organic EL element possessing a structural unit in which organic light-emitting material is gripped between a pair of mutually facing electrodes, at least one of which is transparent or semi-transparent, and a laminate which consists of a protective layer and/or a sealing layer and is provided on the outer side of the structural unit, the laminate's

sealing layer is constituted by a photo-or therm setting resin containing an inorganic composition.

[0022] There is further provided an organic EL element in which the laminate's sealing layer is constituted by a photo-or thermosetting resin containing an inorganic composition.
(Tr. note: Repetition as in text.)

[0023] There is further provided an organic EL element in which the abovenoted inorganic composition is silica glass.

[0024] There is further provided an organic EL element in which, in an organic EL element possessing a structural unit in which organic light-emitting material is gripped between a pair of mutually facing electrodes, at least one of which is transparent or semi-transparent, and a laminate which consists of a protective layer and/or a sealing layer and is provided on the outer side of the structural unit, an organic EL element in which at least one out of the laminate's protective layer and sealing layer comprises at least one organic layer whose oxygen permeability coefficient is $\leq 1 \times 10^{-12}$ cc.cm/cm².S (cmHg).

[0025] There is further provided an organic EL element in which the laminate's protective layer comprises at least one organic layer whose oxygen permeability coefficient is $\leq 1 \times 10^{-12}$ cc.cm/cm².S (cmHg).

[0026] There is further provided an organic EL element in which the laminate's sealing layer comprises at least one organic layer whose oxygen permeability coefficient is $\leq 1 \times 10^{-12}$ cc.cm/cm².S (cmHg).

[0027] There is further provided an organic EL element which further comprises, at the outer side of the laminate's sealing layer, at least one organic layer whose oxygen permeability coefficient is $\leq 1 \times 10^{-12}$ cc.cm/cm².S (cmHg) at the outer side of the laminate's sealing layer.

[0028] There now follows a description of the structure of an organic EL element in which is used in the invention. There is no particular restriction to this structure, but any required structure can be used. For example, one can cite anode/light-emitting layer/cathode, anode/positive hole injection layer/light-emitting layer/cathode, anode/light-emitting layer/electron injection layer/cathode and anode/positive hole injection layer/light emitting layer/electron injection layer/cathode structures. The layers of organic material can be formed by procedure in which a boat containing, eg, the organic substance proposed in Japanese Patent Application Hei No. 5-028659 is heated and vaporized by a resistance heating system using a filament, etc., and the vaporized organic substance is deposited on one of the electrodes. There are no particular restrictions regarding the thickness of the various layers. the thickness of the layers apart from the positive and negative electrodes is usually 5 nm - 5 μ m. Further, there are no particular restrictions regarding the materials as long as they are materials which are normally employed for organic EL elements. Below, a description will be given in relation to an anode/positive hole injection-transport layer/light emitting layer/electron injection-transport layer/cathode organic EL element structure.

[0029] (1) Substrate

It is preferable that the structural unit of the organic EL element which is used in the invention be formed on a substrate. The substrate used in the invention is preferably one which is transparent, and, specifically, one can cite glass, transparent plastic, and quartz, etc.

[0030] (2) Electrodes

The electrodes used in the invention consist of a pair of mutually facing electrodes (anode and cathode), at least one of which is transparent or semi-transparent. It is made transparent or semi-transparent in order to achieve transparency.

(2)-1 Anode

An electrode whose electrode substance is made a large work function ($\geq 4\text{eV}$) metal, alloy, electrically conductive compound or a mixture of these materials can be suitably employed as the anode which is used in the invention. By way of specific examples of such electrode substances, one can cite metals such as Au, etc. and dielectric transparent materials and semi-transparent materials such as CuI, ITO, SnO_2 and ZnO, etc. This anode can be produced by forming such electrode substances as a thin film by procedure such as vapour deposition or sputtering, etc. If emitted light is taken out from this electrode, it is desirable that the electrode's transmittance be greater than 10%. Also, it is preferable that the electrode's sheet resistance be not more than several hundred Ω/\square . Further, although, among other things, it depends on the material, a film thickness in the range 10 nm - 1 μm , preferably 10 - 200 nm can be selected.

[0031] (2)-2 Cathode

The element used for the cathode can be one for which a small work function ($\leq 4\text{eV}$) metal, alloy, electrically conductive compound or a mixture of these materials is made the electrode substance can be used as the cathode. By way of specific examples of such electrode substances, one can cite sodium, sodium-potassium alloys, magnesium, lithium, magnesium/copper mixtures. This cathode can be produced by forming such electrode substances as a thin film by procedure such as vapour deposition or sputtering, etc. It is preferable that the electrode sheet resistance be not more than several hundred Ω/\square , and the film thickness can be selected in a range that is normally 10 nm - 1 μm , and is preferably 50 - 200 nm. Making one or the other out of the anode and cathode transparent or semi-transparent in this organic EL element is desirable for the purpose of increasing the emitted light take-out efficiency by passing emitted light through the actual electrode itself.

[0032] (3) Light-emitting layer

There are no particular restrictions regarding the material of the light-emitting layer, and materials one can cite include benzothiazole, benzimidazole benzoxazole and similar fluorescent brighteners, metal chelate oxinoid compounds and styrylbenzene compounds.

[0033] To give specific compound names, one can cite the compounds noted in the disclosure of Japanese Laid-open Patent Application No. 59-194393. By way of typical examples of these, one can cite, as fluorescent brightening agents, benzoxazole compounds such as 2,5-bis(5,7-di-t-pentyl-2-benzoxazolyl)-1,3,4-thiadiazole, 4,4'-bis(5,7-t-pentyl-2-benzoxazolyl)stilbene, 4,4'-bis[5,7-di-(2-methyl-2-butyl)-2-benzoxazolyl]stilbene, 2,5-bis(5,7-di-t-pentyl-2-benzoxazolyl)thiophene, 2,5-bis[5- α , α -dimethylbenzyl-2-benzoxazolyl]thiophene, 2,5-bis[5,7-di-(2-methyl-2-butyl)-2-benzoxazolyl]-3,4-thiophenylthiophene, 2,5-bis(5-methyl-2-benzoxazolyl)thiophene, 4,4'-bis(2-benzoxazolyl)biphenyl, 5-methyl-2-[2-(4-(5-methyl-2-benzoxazolyl)phenyl)vinyl]benzoxazole, and 2-[2-(4-chlorophenyl)vinyl]naphtho[1,2-d]oxazole, etc., benzothiazole compounds such as 2,2'-(p-phenylenedivinylene)bis-benzothiazole, etc. and benzimidazole compounds such as 2-[2-(4-(2-benzimidazolyl)phenyl)vinyl]benzimidazole and 2-[2-(4-carboxyphenyl)vinyl]benzimidazole, etc. Other useful compounds are listed in Chemistry of Synthetic Dyes, 1971, p.628-637 and p.640.

[0034] The compounds used as the abovenoted chelated oxinoid compounds can, for example, be the compounds noted in Japanese Patent Application No. 63-295695. By way of typical examples of these, one can cite dilithium epinetridione and 8-hydroxyquinoline metal complexes such as tris(8-quinolinol)aluminium, bis(8-quinolinol)magnesium, bis(benzo[f]-8-quinolinol)zinc, bis(2-methyl-8-quinolinolate)aluminium oxide, tris(8-quinolinol)indium, tris(5-methyl-8-quinolinol)aluminium, 8-quinolinol lithium, tris(5-chloro-8-quinolinol)gallium, bis(5-chloro-8-quinolinyl)calcium, and poly-[zinc(II)-bis(8-hydroxy-5-quinolinyl)methane], etc.

[0035] One can, for example, use the compounds disclosed in the Specifications of European Patent Nos. 0319881 and 0373582 as the abovenoted styrylbenzene compounds. Typical examples thereof which can be cited are 1,4-bis(2-methylstyryl)benzene, 1,4-bis(3-methylstyryl)benzene, 1,4-bis(4-methylstyryl)benzene, 1,4-bis(2-ethylstyryl)benzene, 1,4-bis(3-ethylstyryl)benzene, 1,4-bis(2-methylstyryl)-2-methylbenzene, and 1,4-bis(2-methylstyryl)-2-ethylbenzene, etc.

[0036] It is also possible to use, as light-emitting layer materials, the distyrylpyrazine derivatives noted in the disclosure of Japanese Laid-open Patent Application Hei No. 2-252793. Typical examples thereof which can be cited are 2,5-bis(4-methylstyryl)pyrazine, 2,5-bis(4-ethylstyryl)pyrazine, 2,5-bis[2-(1-naphthyl)vinyl]pyrazine, 2,5-bis(4-ethylstyryl)pyrazine, 2,5-bis[2-(1-naphthyl)vinyl]pyrazine, 2,5-bis(4-methoxystyryl)pyrazine, 2,5-bis[2-(4-biphenyl)vinyl]pyrazine, and 2,5-bis[2-(1-pyrenyl)vinyl]pyrazine, etc. Other compounds which can be used as light-emitting layer materials are, eg, the polyphenyl compounds disclosed in the Specification of European Patent No. 0387715).

[0037] Apart from the abovenoted fluorescent brighteners, metal chelate oxinoid compounds and styrylbenzene compounds, other materials which can be used as light-emitting layer materials are, for example, 12-phthaloperinone (J. Appl. Phys., Vol. 27, [713 (1988)], 1,4-diphenyl-1,3-butadiene, 1,1,4,4-tetraphenyl-1,3-butadiene (the above being in J. Appl. Phys. Lett., Vol. 56, L799(1990)), naphthalimide derivatives (disclosure of Japanese Laid-open Patent Application Hei No. 2-305886), perylene derivatives (disclosure of Japanese Laid-open Patent Application Hei No. 1-189890), oxadiazole derivatives (disclosure of Japanese Laid-open Patent Application Hei No. 2-216791, and also the oxadiazole derivatives disclosed by Hamada et al. at the 38th Applied Physics Related Federation Lecture Meeting), aldazine derivatives (disclosure of Japanese Laid-open Patent Application Hei No. 2-220393), pyrazylene derivatives (disclosure of Japanese Laid-open Patent Application Hei No. 2-220394), cyclopentadiene derivatives (disclosure of Japanese Laid-open Patent Application Hei No. 2-289675), pyrrole

derivatives (disclosure of Japanese Laid-open Patent Application Hei No. 2-296891), styrylamine derivatives (Appl. Phys. Lett., Vol. 56, L799 (1990), coumarin compounds (disclosure of Japanese Laid-open Patent Application Hei No. 2-191694), and the high molecular weight compounds described in International Laid-Open Patent Disclosure WO 90/13148 and Appl. Phys. Lett., Vol. 58, 18, P.1982 (1991).

[0038] In the invention, the use of aromatic dimethyldiene compounds (compounds disclosed in the Specification of European Patent No. 038876 and Japanese Laid-open Patent Application Hei No. 3-231970) as light-emitting layer materials is particularly preferred. Specific examples which can be cited are 1,4-phenylenedimethyldiene, 4,4'-phenylenedimethyldiene, 2,5-xylenedimethyldiene, 2,6-naphthylenedimethyldiene, 1,4-biphenylenedimethyldiene, 1,4-p-terphenylenedimethyldiene, 9,10-anthracenediyl dimethyldiene, 4,4'-bis(2,2-di-*t*-butylphenylvinyl)biphenyl, and 4,4'-bis(2,2-diphenylvinyl)biphenyl, etc.

[0039] There are no particular restrictions regarding the thickness of the light-emitting layer which is thus formed and the thickness can be suitably selected in accordance with circumstances, but normally the range 5 nm - 5 μ m is preferable. A light-emitting layer in an organic EL element provides an injection function making possible the injection of positive holes from the anode or a positive hole injection layer and the injection of electrons from the cathode or an electron injection layer when an electric field is imposed, and a transport function whereby injected charges (electrons and positive holes) are moved under the force of an electric field, and it provides a site for the recombination of electrons and positive holes and possesses a light emission function whereby this recombination leads to the emission of light. It is noted that there is not objection if there is a difference between the ease of injection of positive holes and the ease of injection of electrons, but it is preferable that it be possible to cause at least one lot of charges to move.

[0040] (4) Positive hole injection layer

Any materials within materials which are commonly used conventionally as photoconductive material positive hole injection materials and within known materials which are employed for organic EL elements can be selected and used as materials for a positive hole injection layer, which is provided if required. The material of a positive hole injection layer is material which either has a positive hole injection or an electron barrier characteristic, and it may be either organic material or inorganic material.

[0041] By way of specific examples, one can cite, eg, triazole derivatives (see the Specification of US Patent No. 3,112,197), oxadiazole derivatives (see the Specification of US Patent No. 3,189,447), imidazole derivatives (see the disclosure of Japanese Laid-open Patent Application No. 37-16096, etc.), polyaryllalkane derivatives (see the Specifications of US Patent Nos. 3,615,402, 3,820,989 and 3,542,544 the disclosures of Japanese Patent Publication Nos. 45-555 and 51-10983 and the disclosures of Japanese Laid-open Patent Application Nos. 51-93224, 55-17105, 56-4148, 55-108667, 55-196953 and 56-36656, etc.) pyrazoline derivatives and pyrazolone derivatives (see the Specifications of US Patent Nos. 3,180,729 and 4,278,746 and the disclosures of Japanese Laid-open Patent Application Nos. 55-88064 55-88065, 49-105537, 55-51086, 56-80051, 56-88141, 57-45545, 54-11263 and 55-74546, etc.), phenylenediamine derivatives (see the Specification of US Patent No. 3,615,404, the disclosures of Japanese Patent Publication Nos. 51-10105, 46-3712 and 47-25336 and the disclosures of Japanese Laid-open Patent Application Nos. 54-53435, 54-110536 and 54-119925, etc.) arylamine derivatives (see the Specifications of US Patent Nos. 3,567,450, 3,180,703, 3,240,597, 3,658,520, 4,232,103, 4,175,961 and 4,012,376, the disclosures of Japanese Patent Publication Nos. 49-35702 and 39-27577, the disclosures of Japanese Laid-open Patent Application Nos. 55-144250, 56-119132 and 56-22437 and the Specification of West German Patent No. 1,110,518, etc.), amino-substituted chalcone derivatives (see the Specification of US Patent No. 3,526,501), oxazole derivatives (the derivatives disclosed in

the Specification of US Patent No. 3,257,203, etc.), styrylanthracene derivatives (see the disclosure of Japanese Laid-open Patent Application No. 56-46234), fluorenone derivatives (see the disclosure of Japanese Laid-open Patent Application No. 54-110837, etc.), hydrazone derivatives (see the Specification of US Patent No. 3,717,462 the disclosures of Japanese Laid-open Patent Application Nos. 54-59143, 55-52063, 55-52064, 55-46760, 55-85495, 57-11350 and 57-148749, and the disclosure of Japanese Laid-open Patent Application Hei No. 2-311591, etc.), stilbene derivatives (see the disclosures of Japanese Laid-open Patent Application Nos. 61-210363, 61-228451, 61-1642, 61-72255, 62-47646, 62-36674, 62-10652, 62-30255, 60-93445, 60-94462, 60-174749 and 60-175052, etc.), silazane derivatives (Specification of US Patent No. 4,950,950), polysilane derivatives (disclosure of Japanese Laid-open Patent Application Hei No. 2-204996) and aniline copolymers (disclosure of Japanese Laid-open Patent Application Hei No. 2-282263) and the electrically conductive high molecular weight oligomers (especially thiophenone oligomers) disclosed in Japanese Laid-open Patent Application Hei No. 1-211399, etc.

[0042] Although the compounds noted above can be used as positive hole injection layer materials, it is preferable to use porphyrin compounds (compounds described in Japanese Laid-open Patent Application No. 63-2956965, etc.) and aromatic tertiary amine compounds (see the Specification of US Patent No. 4,127,412 and the disclosures of Japanese Laid-open Patent Application Nos. 53-27033, 54-58445, 54-149364, 54-64299, 55-79450, 55-144250, 56-119132, 61-295558, 61-295558, 61-98353 and 63-295695, etc.), especially aromatic tertiary amine compounds.

[0043] By way of typical examples of such porphyrin compounds, one can cite porphin, 1, 10, 15, 20-tetraphenyl-21H, 23H-porphin copper (II), 1,10,15,20-tetraphenyl-21H, 23H-porphin zinc (II), 5,10,15,20-tetrakis(pentafluorophenyl)-21H, 23H-porphin, silicon phthalocyanine oxide, aluminium phthalocyanine oxide, phthalocyanine (nonmetallic), lithium phthalocyanine, copper tetramethylphthalocyanine, copper phthalocyanine, chromium phthalocyanine, zinc phthalocyanine, lead

phthalocyanine, titanium phthalocyanine oxide, Mg phthalocyanine, and copper octamethylphthalocyanine, etc.

[0044] By way typical examples of the abovenoted aromatic tertiary amine compounds and styrylamine compounds, one can cite N,N,N',N'-tetraphenyl-4,4'-diaminophenyl, N,N'-diphenyl-N,N'-bis-(3-methylphenyl)-[1,1',biphenyl]-4,4'-diamine, 2,2-bis(4-di-p-triaminophenyl)propane, 1,1-bis(4-di-p-tolylaminophenyl)cyclohexane, N,N,N',N'-tetra-p-tolyl-4,4'-diaminophenyl, 1,1-bis(4-di-p-tolylaminophenyl)-4-phenylcyclohexane, bis(4-dimethylamino-2-methylphenyl)phenylmethane, bis(4-p-tolylaminophenyl)phenylmethane, N,N'-diphenyl-N,N'-di(4-methoxyphenyl)-4,4'-diaminobiphenyl, N,N,N',N'-tetraphenyl-4,4'-bis(diphenylamino)quadriphenyl, N,N,N-tri(p-tolyl)amine, 4-(di-p-tolylamino)-4'-[4(di-p-tolylamino)styryl]stilbene, 4-N,N-diphenylamino-(2-diphenylvinyl)benzene, 3-methoxy-4'-N,N-diphenylaminostyrylbenzene, and N-phenylcarbazole, etc. Further, the aromatic dimethylidene compounds noted earlier as light-emitting layer materials can also be used as positive hole injection layer materials.

[0045] There are no particular restrictions regarding the thickness of the positive hole injection layer, but it is usually 5 nm - 5 μ m. The positive hole injection layer may be a single-layer structure constituted by one or by two or more of the abovenoted materials, or it may be a multilayer structure consisting of plural layers which have the same composition or have different compositions.

[0046] (5) Electron injection layer

As long as it possesses a function whereby electrons injected from the cathode are transmitted to the light-emitting layer, any known material within compounds which are conventionally known as materials for this purpose may be selected and used for an electron injection layer, which is provided if required.

[0047] By way of specific examples, one can cite nitro-substituted fluorenone derivatives, the anthraquinodimethane derivatives described in the disclosures of Japanese Laid-open

Patent Application Nos. 57-149259, 58-55450 and 63-104061, the diphenylquinone derivatives described in Polymer Preprints, Japan, Vol. 37, No. 3 (1988) p.681, etc. thiopyran dioxide derivatives, heterocyclic tetracarboxylic anhydrides such as naphthaleneperylene, etc., carbodiimides, the fluorenylidene-methane derivatives described in the Japanese Journal of Applied Physics, 27, L269 (1988) and the disclosures of Japanese Laid-open Patent Application Nos. 60-69657, 61-143761 and 61-148159, etc., the anthraquinodimethane derivatives and anthrone derivatives described in the disclosures of Japanese Laid-open Patent Application Nos. 61-225151 and 61-233750, etc., the oxadiazole derivatives disclosed in Appl. Phys. Lett. 55, 15, 1489 and by Hamada et al. at the 38th Applied Physics Related Federation Lecture Meeting), and the series of electron transmitting compounds described in the disclosure of Japanese Laid-open Patent Application No. 59-194393. It is noted that, although these electron transmitting compounds are described as light-emitting layer materials in Japanese Laid-open Patent Application No. 59-194393, investigations by the present inventors made it clear that the compounds can also be used as electron injection layer materials.

[0048] It is also possible to use metal complexes of 8-quinolinol derivatives as electron injection layer materials. Specifically, one can use tris(8-quinolinol) aluminium, tris(5,7-dichloro-8-quinolinol) aluminium, tris(5,7-dibromo-8-quinolinol) aluminium and tris(2-methyl-8-quinolinol) aluminium etc., or metal complexes in which In, Mg, Cu, Ca, Sn or Pb has been substituted for the central metal in the above metal complexes. Other preferred materials are materials which are metal-free, metal phthalocyanines or materials in which the end groups of these materials have been replaced by alkyl groups or sulfonyl groups, etc. Further, the distyrylbenzene derivatives listed as light-emitting layer materials can also be used as electron injection layer materials.

[0049] There are no particular restrictions regarding the thickness of the electron injection layer, but usually it is 5 nm - 5 μ m. The electron injection layer may be a single-layer structure constituted by 1 or 2 or more of the materials noted

above, or it may have a multilayer structure consisting of plural layers which have the same composition or have different compositions.

[0050] Next, laminates (protective layers and/or sealing layers) which are used in the invention will be described in specific detail for respective inventions with reference to the drawings. A protective layer is used for preventing the effects of oxygen and moisture and physical damage at the time of fitting of electrode terminals in the process of organic EL element fabrication, and a sealing layer is used for the purpose of permanent prevention of the effects of external oxygen and moisture.

[0051] 1. 1st Invention

In the organic EL element of the 1st invention, as shown in Fig. 1, a laminate 2 is constituted by the provision of a sealing layer 4 via a protective layer 3 on the outer side of a structural unit 1. The sealing layer 4 is constituted by one or more sets of double layers, each set of which consists of an oxygen absorption layer 41 and an oxygen barrier layer 42. The protective layer 3 and sealing layer 4 will now be described in more specific detail.

[0052] 1) Protective layer

This is not always essential if no harm is caused to the underlying structural unit 1 by the chemical properties of the actual material of the sealing layer 4 or by physical contact at the time of build-up of this layer, but it is preferable to provide it from considerations of keeping damage to the structural unit 1 to a minimum. First, a protective layer constituted by an electrically insulating inorganic compound is provided on the outer surface of the structural unit. It is satisfactory as long as a protective layer is provided on at least the principal outer surfaces of the facing electrodes, but it is particularly preferable to provide it on the entire surface of the structural unit. In the case of an organic EL element with a structure in which the facing electrodes are provided on portions of a light-emitting layer,

positive hole injection layer or electron injection layer, it is preferable that there be provision of a protective layer at least on the facing electrodes and on these portions, within the principal surfaces of layers constituting facing electrode underlayers, on which the facing electrodes are not provided. It is satisfactory as long as the insulating organic compound constituting the material of the protective layer is insulating material which can be made a film by physical vapour deposition (sometimes referred to below as PVD), specific examples one can cite being oxides such as MgO, GeO, Al₂O₃, NiO, CaO, BaO, Fe₂O₃, Y₂O₃, SiO₂ and titanium oxide, etc., nitrides such as AlN, BN, Si₃N₄ and Li₃N, etc., sulfides such as SrS, EuS, CuS and ZnS, etc., and various electrically insulating inorganic compounds such as MgF₂, Mg(OH)₂ and BaSO₄, etc. Within these insulating inorganic compounds, metal oxides such as GeO, MgO, Al₂O₃ and NiO, etc. which can be made films by reactive vapour deposition, etc. in comparatively mild conditions are particularly preferred.

[0053] A protective layer constituted by an insulating inorganic compound can be produced by PVD procedure suitable for the inorganic compound which is used. If the side on which the protective layer is provided is a light-emitting surface, a material and a formation method such as to produce a protective layer which has excellent transparency with respect to EL light from the organic EL element are selected. A variety of procedures are known as PVD procedures, but preferably vacuum vapour deposition procedure or sputtering procedure is used. These procedures can, for example be subdivided in the manner noted below, and any one of these procedures can be employed.

a. Vacuum vapour deposition

Resistance heating procedure, electron beam heating procedure, high-frequency induction heating procedure, reactive vapour deposition procedure, hot-wall vapour deposition procedure, ion plating procedure, cluster ion beam procedure, etc.

b. Sputtering procedure

2-Electrode sputtering procedure, 2-electrode magnetron sputtering procedure, 3-electrode and 4-electrode plasma sputtering procedure, ion beam sputtering procedure and methods combining these procedures, etc.

[0054] Preferably, the formation of the protective layer is effected in a manner such as not to cause degeneration of the organic material constituting the structural unit on which the protective layer is to be provided. The conditions for avoiding degeneration of organic material constituting the structural unit vary depending on the type of this material, ie, on its heat resistance and other properties, but, generally, it is preferable to keep the temperature of the organic material to 200°C or less and it is still more preferable to keep its temperature to 100°C or less. There is, of course, no restriction to this if materials such as high molecular weight compounds which are strongly resistant to heat are used for the light-emitting layer, etc. There now follows a description of preferred formation conditions in the various procedures.

(1) Vacuum vapour deposition procedures

The preferred procedures within these procedures are those of reactive vapour deposition and electron beam deposition. To take, as an example, the case in which a protective film of a metal oxide (MgO) is formed by reactive vapour deposition procedure, it is best to make the deposition time ≤ 2 hours, preferably ≤ 1 hour, and still more preferably ≤ 20 minutes. Preferably, the degree of vacuum in the vacuum chamber before deposition is made 1×10^{-2} Pa or less, 6×10^{-3} Pa or less being particularly preferred, following which the pressure in the vacuum chamber is made 7×10^{-3} Pa or more, preferably 1×10^{-2} or more in the stage in which oxygen and/or steam is introduced, and then metallic Mg constituting the vapour deposition source material is heated to $\leq 100^\circ\text{C}$ and vapour-deposited. The deposition rate is preferably 10 nm/second or less, 3 nm/second or less being particularly preferred.

(2) Sputtering procedures

With sputtering, since material it is wished to deposit is expelled from a target by ions, the energy is generally higher than in vacuum vapour deposition. In other words, the conditions are severer than in vacuum vapour deposition. Particularly preferred procedures within sputtering procedures are those of reactive sputtering and ion beam sputtering. To take, as an example, the case in which a protective film of MgO is formed by reactive ion beam sputtering (in which metallic Mg is sputtered and oxidized by an oxygen ion beam), it is best if the deposition time is 1 hour or less, preferably 30 minutes or less, and still more preferably 10 minutes or less. ≤ 1200 V, especially ≤ 600 V is preferable as the oxygen ion beam acceleration voltage, and ≤ 500 mA, especially ≤ 60 mA is preferred as the beam current.

[0055] The thickness of the protective layer formed in the above manner is determined by a balance between the deposition rate and the deposition speed. The thicker the protective layer is the greater its effects can be expected to be, but producing a thick protective layer necessitates making the deposition time long or making the deposition rate fast, and this results in greater damage to organic material in the structural unit. It is therefore necessary to set an upper limit for the thickness of the protective layer. For example, if an MgO film is formed by reactive vapour deposition procedure, since organic material suffers considerable damage if the film is formed at the maximum deposition rate (10 nm/second), the deposition time in this case must be made not more than 20 minutes. The upper limit value of the film thickness in this case is about 12 μm . On the other hand, the lower limit for the thickness of the protective layer is determined with reference to whether or not the layer has a protection effect, and, generally, if the layer is less than about 10 nm, it is too thin and fails to function satisfactorily as a protective layer. From the point of view of producing a long-life organic EL element, it is desirable to suppress, as much as possible, deterioration of the properties of the light-emitting layer and facing electrodes.

during the protective layer formation process, and it is therefore preferable to form the protective layer in a vacuum environment. For similar reasons, it is particularly preferable that the processes from formation of a light-emitting layer for constituting the structural unit to formation of the protective layer be conducted in a series of vacuum environments.

[0056] By way of other materials for the protective layer in the invention, it is also possible to use electrically insulating high polymers. It is satisfactory if these insulating high polymer compounds are materials which can be made films by physical vapour deposition procedure (which is sometimes called 'PVD procedure' below) or chemical vapour deposition procedure (which is sometimes called 'CVD procedure' below) or are soluble in an organic solvent such as a perfluoro alcohol, perfluoro ether or perfluoro amine, etc., and material with low humidity permeability is particularly preferred. The following substances can be cited as specific examples of insulating high polymer compounds.

[0057] (1) Electrically insulating high polymer compounds which can be made films by PVD procedure

Polyethylene, polypropylene, polystyrene, polymethacrylate, polyimide (material in which two types of monomers are deposited on a substrate and polymerized; see Technical Journal, 1988, 30, 22), polyurea (material in which two types of monomers are deposited on a substrate and polymerized; see Technical Journal, 1988, 30, 22), the fluorine-based high polymer compounds described in the disclosure of Japanese Laid-open Patent Application No. 63-18964, the fluorine-based high polymer compounds described in the disclosure of Japanese Laid-open Patent Application No. 63-22206, the fluorine-based high polymer compounds described in the disclosure of Japanese Laid-open Patent Application No. 63-238115, polytetrafluoroethylene, polychlorofluoroethylene, polydichlorodifluoroethylene, chlorotrifluoroethylene and dichlorodifluoroethylene copolymers and fluorine-containing copolymers possessing a cyclic structure (see Japanese Patent Application Hei No. 3-129852).

[0058] (2) Electrically insulating high polymer compounds which can be made films by CVD procedure (plasma polymerization procedure (plasma CVD))

Polyethylene, polytetrafluoroethylene, polyvinyltrimethylsilane, polysiloxane, etc.

[0059] (3) Electrically insulating high polymer compounds which are soluble in fluorine-based solvents such as perfluoro alcohol, perfluoro ether, perfluoro amine, etc.

Fluorine-based high polymer compounds such as the fluorine-based high polymer compounds described in the disclosure of Japanese Laid-open Patent Application No. 63-18964, the fluorine-based high polymer compounds described in the disclosure of Japanese Laid-open Patent Application No. 63-22206, the fluorine-based high polymer compounds described in the disclosure of Japanese Laid-open Patent Application No. 63-238115, polychlorotrifluoroethylene, polydichlorodifluoroethylene, chlorotrifluoroethylene and dichlorodifluoroethylene copolymers and fluorine-based high polymer compounds possessing a heterocyclic structure (see the disclosure of Japanese Laid-open Patent Application Hei. No. 3-129852), etc.

[0060] Depending on the high polymer compound used, the protective layer can be produced by PVD procedure (the high polymer compounds of (1) above), by CVD procedure (the high polymer compounds of (2) above) or by casting or spin coating procedure (the high polymer compounds of (3) above). The thickness of the protective layer in this case depends on the material used and the forming method among other things but is preferably 10 nm - 100 μ m. If the side on which the protective layer is provided is a light-emitting surface, material and a formation method such as to produce a protective layer which has excellent transparency with respect to EL light from the organic EL element is selected. Protective layer formation by the various methods can, for example, be effected in the following manner.

- For PVD procedure, one can employ the same procedure as used for inorganic insulating high polymer compounds. The film formation conditions vary depending on the raw material and the type of PVD procedure employed, but in the case of,

eg, vacuum vapour deposition (resistance heating method, electron beam heating method, high-frequency induction heating method), it is desirable to effect film formation with the degree of vacuum before deposition made about 1×10^{-2} Pa or less, preferably 6×10^{-3} Pa or less, the temperature to which the deposition source is heated made about 700°C or less, preferably 600°C or less, the substrate temperature made about 200°C or less, preferably 100°C or less, and the deposition rate made ≤ 50 nm/second, preferably ≤ 3 nm/second.

[0061]- CVD procedure

Plasma polymerization in which polymerization is effected by making gaseous monomers of ethylene and propylene, etc. plasmas is preferable. Generally, pyrolysis process CVD is unsuitable, since the substrate temperature becomes high.

[0062] - Casting procedure

A protective layer is produced by dissolving the source material in a fluorine-based solvent such as a perfluoro alcohol, perfluoro ether or perfluoro amine, etc., spreading the resulting solution on the structural unit and then air-drying it for 8-16 hours. The drying time may be any duration as long as it is 8 hours or more, but it is unsuitable to dry the material for more than 16 hours, since, even if this is done, it does not result in any great difference in the degree of drying. Usually, a drying time of about 12 hours is suitable. The concentration of the source material in the solution is suitably selected in accordance with the target protective layer thickness.

[0063] - Spin coating procedure

A protective layer is produced by a process in which a suitable quantity of a solution produced in the same way as in the casting procedure described above is applied dropwise on a structural unit which is being rotated at 100-20000 rpm, preferably 200-8000 rpm, the structural unit continues to be rotated in the same manner for a further 5-30 seconds, and then drying is effected in the same way as in casting

procedure. The amount of solution applied dropwise in this process varies depending on the size of the structural unit or of the organic EL element it is intended to seal, but in the case of a structural unit or an organic EL element with an ordinary slide glass size (25 x 75 x 1.1 mm), the amount is 0.6 - 6 ml, preferably 0.5 - 3 ml. The concentration of the source material is the solution can be suitably selected in accordance with the target protective layer thickness, as in casting procedure, but its range is narrower than it is in the case of casting procedure, and from consideration of aspects such as film thickness control and film uniformity, etc. it is 1 - 40 g/100 ml, preferably 4 - 20 g/100 ml.

[0064] Both in casting procedure and in spin coating procedure, it is preferable that air drying be followed by further drying, by means of vacuum drier, etc., for 1-24 hours, preferably 8-16 hours at 30-100°C, preferably 50-80°C.

[0065] (2) Sealing layer

(1) Structure: Going from the side nearer the cathode 13 of the structural unit 1, one or more sets of double layers possessing an oxygen absorption layer 41 and an oxygen barrier layer 42 in that order are deposited on the protective layer 3.

(2) Film thickness: Preferably one set is from several to several hundred μm .

(3) Deposition method: Preferably, use is made of a deposition method with which damage to the structural unit at the time of deposition is suppressed as much as possible. One can use deposition procedures which are the same as those employed for the protective layer. In addition, dip procedures and spin coating procedures, etc. which are known as high polymer coating methods can be used.

(4) Oxygen absorption layer: By way of materials which can be used for the oxygen absorption layer 41, one can cite (i) organic compounds with a low ionization potential, eg, positive hole transport materials of electronic photopying

photosensitive bodies, amine compounds and hydrazone compounds, etc., (ii) oxygen adsorbing compounds, (iii) fluorine compound, eg, fluorine-based hydrocarbon inert solutions, etc., and (iv) metals in powder form, eg, Fe, C, Ni, Cu, alkali metals or alkaline earth metals with a particle diameter of about several μm and low work function metals, eg, Al, In, Mg, Yb, Zr, Na and K, etc. Forms of the oxygen absorption layer which can be cited are that of simple substances as noted above in solid form (vapour-deposited film, sputtered film, etc.) or that of a film of a dispersion in a liquid or a high polymer (butyral resin, PC, PS, etc.).

(5) Oxygen barrier layer

By way of materials for constituting an oxygen barrier layer, one can cite the metal oxides, nitrides and fluorides which are used for the protective layer, substances which are known to have a low oxygen permeability coefficient, eg, polyvinyl alcohol, butyl rubber, polyethylene, polynitrile resin, polyvinylidene chloride (saran), nylon-6 and similar polyamide resins, etc. and Si nitrides, etc. which are known as passivation films for semiconductor elements. Forms of the oxygen barrier layer one can cite are those of vapour-deposited and sputtered films of the abovenoted substances and high polymer coating films, etc.

(6) If required, there may be further provision of a frame 5 of glass or resin at the outer side of the sealing layer 4.

[0066] 2. 2nd Invention

The special feature of the organic EL element and the 2nd invention is that, as illustrated in Fig. 2, at least one of the protective layer 3 and sealing layer 4 of the laminate 2 contains material 6 which adsorbs, occludes or consumes oxygen. In this 2nd invention, there is no need to make a strict distinction between the protective layer and the sealing layer. If a solid substance is used for the sealing layer, it is preferable to use a bonding layer 7 in order to effect stronger sealing on the substrate. The sealing layer may also serve jointly as a bonding layer. As the result of material which adsorbs, occludes or consumes oxygen being

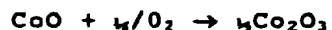
included in a layer which is one or the other of the protective layer and sealing layer (and which is referred to below as protective sealing layer 2'), trace amounts of oxygen inside the element are adsorbed, occluded or consumed, and the effects of oxygen on the electrodes and organic material are prevented. Material by which oxygen is adsorbed, etc. may also be included in the bonding layer. The form of adsorption of oxygen may be physical adsorption or chemical adsorption. What is meant by occlusion of oxygen is that oxygen is taken in and held physically or chemically. Forms of this one can cite are, eg, clathration, intercalation and adsorption, etc. What is meant by consumption of oxygen is the consumption of oxygen through a chemical reaction. Forms of this one can cite are, eg, the oxygen of hydration, peroxidation and the production of hydroxides, etc. and coordination. There are no particular restrictions regarding the form of the protective sealing layer as long as it is a layer which can cover the substrate or structural unit. If the protective sealing layer is in the form of a sheet of metal or is a thin film of metal, a resin film, a resin moulding or a glass product, an oxygen adsorbent, etc. may be made microcapsules and coated on or vapour-deposited. If the protective layer and sealing layer are provided separately as two layers, the material may be provided between them. Alternatively, if the protective sealing layer is constituted by material which is in gel form, or semi-milled form or is a liquid, an oxygen adsorbent, etc. can be used by being mixed with and dispersed in this raw material. An oxygen adsorbent, etc. can also be used by being mixed with and dispersed in the raw material if a thermosetting resin, photosetting resin or reactive resin, etc is used to produce the protective sealing layer. A variety of adhesives can be used if the protective sealing layer is bonded to the substrate. An oxygen adsorbent, etc. may be used mixed with the adhesive. Preferably the content of oxygen adsorbent, etc. is ≤ 10 wt% in the protective sealing layer. If it exceeds 10 wt%, the uniformity of the protective sealing layer may be adversely affected. 0.01 - 5% is still more preferable.

[0067] The following substances can be cited as materials which adsorb, occlude or consume oxygen.

(1) Material constituted by one or more substances selected from among magnesium oxide, magnesium carbonate, iron oxide, titanium oxide, bentonite, acidic clay, montmorillonite, kieselguhr (clay mineral), activated alumina, silica-alumina, zeolite, silica, zirconia and activated carbon (preferably material which has been calcined at $\geq 120^{\circ}\text{C}$ in an inert gas).

[0068] (2) Fine powder, thin films, salts or oxides of metals of the 4th period of the periodic table (Fe, Co, Ni, Cr, V, Zn, Cu) and material in which a metal of the 4th period of the periodic table (Fe, Co, Ni, Cr, V, Zn, Cu) or a salt or oxide thereof is carried by one or more substances selected from among magnesium oxide, magnesium carbonate, iron oxide, titanium oxide, bentonite, acidic clay, montmorillonite, kieselguhr (clay mineral), activated alumina, silica-alumina, zeolite, silica, zirconia and activated carbon (preferably material which has been calcined at $\geq 120^{\circ}\text{C}$ in an inert gas).

The concentration carried is preferably ≤ 10 wt%, and still more preferably it is ≤ 5 wt%. One can, for example, cite cobalt oxide (II) CoO crystals. This material is a crystalline compound which absorbs oxygen, and it reacts with oxygen by the following formula.



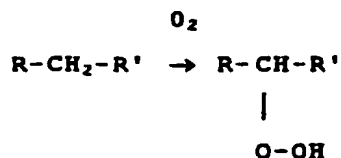
[0069] (3) Material in which a 3-30C primary or secondary carbon-possessing hydrocarbon, eg, an alkylcyclohexane, alkane, alkene or cumene, etc. is impregnated at a concentration of ≤ 1 wt% in activated carbon, or in a fine powder or thin film of a metal of the 4th period of the periodic table or a salt or an oxide of this metal, or in material in which a fine powder or thin film of a metal of the 4th period of the periodic table or a salt or an oxide of this metal is carried at a concentration of ≤ 10 wt% on one or more substances selected from the group consisting of magnesium oxide, magnesium carbonate, iron oxide, titanium oxide, bentonite, acidic clay, montmorillonite, kieselguhr (clay mineral), activated alumina, silica-alumina, zeolite, silica, zirconia and activated carbon.

[0070] (4) Material in which platinum, palladium, ruthenium or tin is carried at a concentration which is preferably ≤ 5 wt% (and which still more preferably is ≤ 1 wt%, ≥ 0.001 wt%) on one or more substances selected from the group consisting of magnesium oxide, magnesium carbonate, iron oxide, titanium oxide, bentonite, acidic clay, montmorillonite, kieselguhr (clay mineral), activated alumina, silica-alumina, zeolite, silica, zirconia and activated carbon.

[0071] The reasons why such substances can be suitably employed in the invention will now be described. In the case of (1), compounds with a large surface area have the ability to adsorb oxygen and molecules of organic substances. In the case of (2), oxygen is consumed through oxidation of the metals themselves by oxygen. Further, the metals, metal salts and metal oxides have the ability to adsorb oxygen. In the case of cobalt oxide (II), use is made of a reaction whereby the crystals absorb oxygen and become other crystals. In the case of (3), the metals display a catalytic action as the result of the presence of alkanes or alkenes, and consume oxygen through reactions such as indicated in the formulas below. Metals carried on inorganic substances are particularly superior, since, with these, oxygen is also adsorbed by their reaction products and so oxygen is not expelled to outside the system.

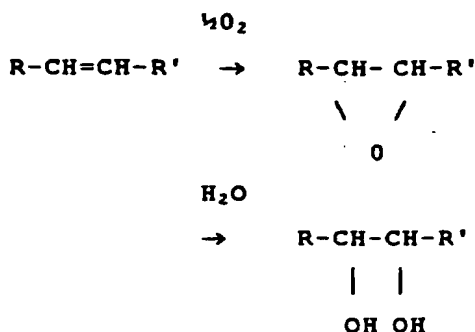
[0072]

[Formula 1]



{0073}

[Formula 2]



(Tr. note: Please see text sheet 12 sections [0072], [0073] for the precise form of formulas 1 and 2.)

[0074] In the case of (4), there is the same ability as in (2) and (3). Use of activated carbon as a carrier is particularly effective, since this has a large surface area. Further, the reaction



takes place, and oxygen is adsorbed directly by the activated carbon.

[0075] 3. 3rd Invention

The protective layer used in the 3rd invention contains a dehydrating agent 31, as indicated in Fig. 3. As long as it is material which is a solid at room temperature, there are no particular restrictions regarding the base material of the protective layer 3 which is used in the 3rd invention, and use may be made of, eg, polyolefin, polyether, polycarbonate, polyamide or similar polymers, amorphous organic material such as Teflon AF (tradename; product manufactured by Du Pont Corporation) or inorganic material such as α -Si : α -SiC, α -C or GeO, etc. Within these materials, Teflon AF is particularly preferred. There are no particular restrictions regarding the method of producing the protective layer, and methods which can be cited are, eg, coating, vapor deposition, spin coating, sputtering and CVD, etc., but spin

coating is preferred, since organic luminescent material is weak against heat. The material used as the dehydrating agent 31 which is included in the protective layer can be, eg, a salt anhydride (anhydrous magnesium sulfide, anhydrous lithium chloride, etc.) a chloride (calcium chloride, lithium chloride, etc.), an oxide (calcium oxide, etc.), silica gel, zeolite, a molecular sieve, activated carbon or graphite, etc. but alkali metals and alkaline earth metals (sodium, potassium, calcium, magnesium, etc.) are particularly preferred. The dehydrating agent content is ≤ 10 wt% in the protective layer. A dehydrating agent to an amount exceeding 10 wt% sometimes causes the protective layer to become unstable. It is noted that there may be further provision of a sealing layer etc. on the outer side of the protective layer 3 containing a dehydrating agent 31.

[0076] 4. 4th Invention

The sealing layer used in the 4th invention is constituted by a photo- or heat-curable resin layer 43 containing an inorganic composition 44, as indicated in Fig. 4. If required, another sealing layer may be deposited on this sealing layer 4. Further, a protective layer may be provided underneath the sealing layer 4. Fine metal particles and inorganic oxide particles can be cited as the inorganic composition 44. Specifically, one can cite particles of alumina, silica glass, colloidal silica, borosilicate glass, β -eucryptite, barium glass, silicon nitride, beryllium nitride and silicon carbide, etc. Such inorganic compositions are preferably in a compositional ratio ≥ 50 wt%, ≤ 95 wt% relative to the entirety of the sealing layer, a compositional ratio of ≥ 60 wt%, ≤ 85 wt% being still more preferable. There are no particular restrictions regarding the photosetting resin, but the composition before curing is preferably one which comprises at least a polyfunctional monomer, a photo-polymerization initiator (a photosensitizer), a reducing agent and a polymerization inhibitor, etc. There are no particular restrictions regarding the light wavelength region, but material containing components which react in the visible light region (380-650 nm) is preferred. Control of the

sealing layer 4 by means of the abovenoted composition makes it possible to form a uniform film and to control the shrinkage ratio and the coefficient of thermal expansion at the time of curing (polymerization) and so suppress deterioration associated with stress imposed on the element. As noted above, the arrangement may also be that another sealing layer is provided on the sealing layer 4 constituted by a photosetting resin layer 43 containing an inorganic composition 44. By way of another sealing layer, one can cite, eg, an oxygen barrier layer, a water-repellent layer and a moisture-absorbing layer, etc. Since the abovenoted photo- or thermosetting resin is fluid prior to curing, it is possible to change the shape of the back surface in accordance with the conditions of placement of the organic EL element.

For this purpose, material which possesses initial fluidity and can be made solid by suitable treatment or a film possessing pliability is also preferable in the case where another sealing layer as noted above is provided. Examples one can give of such photosetting resin or thermosetting resin are butyl rubber resin, ethylene-butadiene rubber resin, styrene-butadiene rubber resin, chloroprene resin, acrylic resin, epoxy resin, fluororesin and silicone resin, etc. Further, it is preferable that these materials be materials which are excellent in respect of electrical insulation and which do not produce side products at the time of curing, given which, epoxy resin and silicone resin are particularly preferred.

[0077] 5. 5th Invention

As indicated in Fig. 5, the laminate used in the 5th invention is constituted by at least one organic layer 22 whose oxygen permeability coefficient is $\leq 1 \times 10^{-12}$ cc.cm/cm².s (cmHg). Preferably, there is further provision of a water-resistant layer deposited on or below this organic layer 22. There may also be provision of a protective layer below the organic layer 22. Apart from the specific example shown in Fig. 5, the structure may also be made as shown in Fig. 6 and Fig. 7. Procedures one can cite for measuring the oxygen permeability coefficient include eg, the method described in Kobunshi Kagaku (Polymer Chemistry), Vol. 16, No. 168 (1959).

and the method described in J. Polym. Sci., Part 2A-2, Vol. 8, p.467 (1970). By way of specific materials, one can cite thin films of polyvinylidene chloride (tradename: Saran), polyvinyl chloride, polyvinyl alcohol, cellulose, cellophane and acetic acid fibre, etc. There are no particular restrictions regarding the film formation method, and one can use methods such as vapour deposition, polymerization, sputtering, casting and spin coating, etc. By way of another method, the procedure may be that of hot pressure bonding of a material as noted above. If a wet process (eg, a casting or spin coating process) is used, it is preferable to form the film after a water-resistant and chemical-resistant sealing layer has been formed beforehand. Although descriptions have been given above with reference to individual inventions, the 1st to 5th inventions may be suitably combined.

[0078]

[Examples of implementation] The invention will now be described in more specific detail by means of examples of implementation thereof.

[EXAMPLE 1]

Fabrication of organic EL element structural unit

A glass plate (white sheet glass manufactured by the HOYA Company) with a size of 25 x 75 x 1.1 mm was used as a substrate, and an ITO film was formed to a thickness of 100 nm on this substrate to constitute a transparent electrode. (Below, a substrate on which an ITO film has been formed will be called a transparent support substrate.) 30 minutes ultrasonic cleaning of this transparent support substrate was effected in isopropyl alcohol, and this was followed by 5 minutes washing with pure water, then rinsing with isopropyl alcohol, and then drying by blow-on of dry N₂ gas. Finally, 10 minutes cleaning was effected in a UV ozone cleaning unit (manufactured by Samco [Tr. note: Transliteration] International). Having been cleaned, the transparent support substrate was fixed to the substrate holder of a commercially available vacuum vapour deposition unit (manufactured by the Nihon Shinku Gijutsu Company), 200 mg of N,N'-diphenyl-N,N'-

bis-(3-methyphenyl)-[1,1'-biphenyl]-4,4'-diamine (referred to below as TPD) was put into a resistance heating boat made of molybdenum, 200 mg of tris(8-quinolinol) aluminium (referred to below as Alq.) was put into another resistance heating boat made of molybdenum, and the pressure in the vacuum chamber was reduced to 1×10^{-4} Pa.

[0079] Next, the resistance heating boat into which TDP had been put was heated to 215-220°C, and the TDP was deposited on the ITO film of the transparent support substrate at a vapour deposition rate of 0.1 - 0.3 nm/second, so forming a positive hole injection layer with a film thickness of 60 nm. The substrate temperature at this time was room temperature. Next, while the transparent support substrate on which the positive hole injection layer had been formed was still fixed to the substrate holder, the molybdenum resistance heating boat into which Alq. had been put was heated to 275°C, and the Alq. was deposited on the positive hole injection layer at a vapour deposition rate of 0.1 - 0.2 nm/second, so forming a light-emitting layer with a film thickness of 60 nm. The substrate temperature at this time too was room temperature. Next, a molybdenum resistance heating boat into which 1 mg of magnesium (Mg) had been put beforehand and a molybdenum resistance heating boat into which 500 mg of silver (Ag) had been put beforehand were each heated to effect vapour deposition of Mg at a vapour deposition rate of 1.6 nm/second and, simultaneously, vapour deposition of Ag at a vapour deposition rate of 0.1 nm/second and so form, on the light-emitting layer, an electrode (facing electrode) with a film thickness of 160 nm which consisted of a metal mixture of Mg and Ag. This provision of an ITO film (electrode), positive hole injection layer, light-emitting layer and facing electrode on the glass substrate resulted in the production of an organic EL element. In this structural unit, a laminate structure was formed by the ITO film, positive hole injection layer, light-emitting layer and facing electrode. At this stage, leads were taken out from the ITO and the Mg:Ag surface which was not above the ITO. In this state, the unit was returned again to the vacuum chamber, and the pressure was reduced to 1×10^{-4} Pa.

[0080] Formation of protective layer

Oxygen was introduced into the vacuum chamber and the pressure in the vacuum chamber was made 8×10^{-3} Pa. Next, the molybdenum resistance heating boat into which Mg had been put (the boat of the time of production of the facing electrode) was heated to 485°C to cause Mg to be vapour-deposited at a vapour deposition rate of 0.5 nm/second and at the same time react with oxygen in the vacuum chamber, so producing an MgO film (protective layer) with a film thickness of $0.3 \mu\text{m}$ (300 nm) on the outer surface of the laminate structure.

[0081] Formation of oxygen absorption layer, oxygen barrier layer

After that, the pressure was reduced again to 1×10^{-4} Pa, and Mg was vapour-deposited at a vapour deposition rate of 1 nm/second to constitute a $0.5 \mu\text{m}$ oxygen absorption layer. After that, $0.5 \mu\text{m}$ deposition and film formation of MgO was effected by the same procedure to constitute an oxygen barrier layer. After the build-up to the abovedescribed sealing layer, the element was caused to emit light.

Voltage (V)	6
Current density (mA/cm ²)	10.3
Luminance (cd/m ²)	290
Luminous efficiency (lm/W)	1.47

The uniformity in the light emission plane (0.3 cm^2) was quite good, only 5 non-emitting points being observed in an image at a magnification of 10 x. It was found from the results with Comparison Example 1, which is described below, that the build-up of the protective layer and sealing layer did not adversely affect the light emission performance or the uniformity of light emission.

[0082] [EXAMPLE 2] On the MgO (oxygen barrier layer of Example 1), Mg and MgO were deposited as a 2nd repeating unit by the same method and to the same film thickness. The element performance after completion of sealing was practically the same as in Example 1, being as follows.

Voltage (V)	6
Current density (mA/cm ²)	10.0
Luminance (cd/m ²)	270
Luminous efficiency (lm/W)	1.45
Number of non-emitting points	7

*Below, examination of images at a magnification of 10 x, as in Example 1.

[0083] [EXAMPLE 3] Instead of the Mg of the oxygen absorption layer of Example 1, a film in which Fe fine powder was dispersed in Polycarbode [Tr. note: transliteration] resin (Pc) was deposited to 100 μ m by the following procedure. The average particle diameter of the Fe was 5 μ m, and, with the dispersion concentration made Pc : Fe = 50 : 30 wt%, a film was formed from a CH₂Cl₂ solution by dip coating procedure. Next, for the oxygen barrier layer, high-density polyethylene (tradename : 440M; manufactured by Idemitsu Sekiyu Kagaku KK) was charged into an alumina crucible and deposited to 10 μ m by vacuum vapour deposition procedure in a vacuum of 1×10^2 Pa (crucible temperature: 370°C). The element performance after completion of sealing was similar to that in Examples 1 and 2, being as follows.

Voltage (V)	6
Current density (mA/cm ²)	10.5
Luminance (cd/m ²)	287
Luminous efficiency (lm/W)	1.43
Number of non-emitting points	8

[0084] [COMPARISON EXAMPLE 1] An organic EL element was fabricated by procedure that was the same as in Example 1 except that a protective layer and sealing layer (oxygen absorption layer and oxygen barrier layer) were not provided. The element performance was as follows.

Voltage (V)	6
Current density (mA/cm ²)	10.6
Luminance (cd/m ²)	304
Lumin us efficiency (lm/W)	1.50

Number of non-emitting points

3

[0085] [COMPARISON EXAMPLE 2] An organic EL element was fabricated by procedure which was the same as in Example 1 except that only a protective layer was deposited. The light emission performance was approximately the same as in comparison Example 1.

Voltage (V)

6

Current density (mA/cm²)

10.5

Luminance (cd/m²)

300

Luminous efficiency (lm/W)

1.50

Number of non-emitting points

4

[0086] Confirmation of dark spot suppression effect

After the elements had been fabricated, changes in the uniformity of the light emission surfaces as the result of constant-current continuous drive were investigated at room temperature (23°C) in air. The numbers of non-emitting points 1000 hours after element manufacture were as noted below. For both the examples of the invention and the comparison examples, observations were made in a field of view at a magnification of 10 x. The figures in brackets indicate the increases in the values from the initial-period values.

Example 1	10 (5)
Example 2	11 (4)
Example 3	9 (1)
Comparison Ex. 1	105 (92)
Comparison Ex. 2	70 (66)

It was seen from these results that the occurrence of non-emitting points is effectively suppressed by the sealing layer consisting of oxygen absorption layer and oxygen barrier layer.

[0087] Confirmation of suppression of fall of luminance

Changes in the luminance from an initial-period luminance of 100 cd/m² as the result of constant-current continuous drive were measured at room temperature (23°C) in air.

	Luminance half-life time (hours)	Element breakdown time (hours)
Example 1	4,600	15,000
Example 2	9,300	20,000
Example 3	7,500	17,000
Comparison Ex. 1	212	953
Comparison Ex. 2	508	12,000

It was learned that a fall in luminance is effectively suppressed by the sealing layer consisting of an oxygen absorption layer and oxygen barrier layer.

[0088] [EXAMPLE 4]

Fabrication of organic EL element structural unit

A substrate in which an ITO electrode had been made a film with a thickness of 100 nm on a glass substrate shape with a size of 25 mm x 75 mm x 1.1 mm was taken as a transparent support substrate. This was subjected to 30 minutes ultrasonic cleaning in isopropyl alcohol and then washed for 30 minutes with pure water, and, finally, 30 minutes ultrasonic cleaning in isopropyl alcohol was effected again. Then the transparent support substrate was fixed to the substrate holder of a commercially available vapour deposition unit (manufactured by Nihon Shinku Gijutsu), 200 mg of N, N'-diphenyl-N-N'-bis-(3-methylphenyl)-[1,1'-biphenyl]-4,4'-diamine (TPD) was put into a resistance heating boat made of molybdenum, 200 mg of tris(8-quinolinol) aluminium (Alq.) was put into another resistance heating boat made of molybdenum, and the pressure in the vacuum chamber was reduced to 1×10^{-4} Pa. After that, the boat containing TDP was heated to 215-220°C and TPD was deposited on the substrate at a vapour deposition rate of 0.1 - 0.3 nm/second, so forming a positive hole injection layer with a film thickness of 60 nm. The substrate temperature at this time was room temperature.

With ut this element being taken out of the vacuum chamber, Alq. from the ther boat was vap ur-dep sited to 60 nm to constitute a light-emitting layer on the p sitive h le injection layer. The vapour deposition conditions were that the boat temperature was 275°C, the vapour deposition rate was 0.1-0.2 nm, and the substrate temperature was room temperature. Next, lg of magnesium was put into a resistance heating boat made of molybdenum, and 500 mg of indium was put into another resistance heating boat made of molybdenum. After that, the pressure of the vacuum chamber was reduced to 2×10^{-4} Pa, indium was vapour-deposited at a vapour deposition rate of 0.03 - 0.08 nm/second, and, at the same time, magnesium was vapour-deposited from the other boat at a vapour deposition rate of 1.7 - 2.8 nm/second. The magnesium and indium boat temperatures were respectively about 500°C and 800°C. In these conditions, a magnesium and indium metal mixture electrode was vapour-deposited to 150 nm on the light-emitting layer to constitute a facing electrode. This produced an organic EL element structural unit with an ITO/TPD/Alq/Mg:In structure. The initial performance of this organic EL element was that, with the voltage at 7 V, the current density at 3.6 mA/cm² and the luminance at 105 cd/m², the power conversion efficiency was 1.3 m/W.

[0089] Formation of protective sealing layer

A solution in which 50 g of a tetrafluoroethylene and perfluoro-2,2-dimethyl-1,3-dioxole amorphous copolymer powder (tradename: Teflon AF No. 1600; manufactured by the Du Pont Corporation) was dissolved in 100 ml of Florinate [Tr. note: Transliteration] FC 48 (tradename; manufactured by the Sumitomo 3M Company) was put into a glow box through which nitrogen gas was flowed, and lg of activated carbon (manufactured by the Wako Junyaku Company) carrying 5 wt% of platinum was made a powder in a mortar and then added and dispersed by stirring. Next, the resulting solution was coated on the abovedescribed structural unit to produce a cast film and constitute a protective sealing layer (film thickness 10 microns).

[0090] [EXAMPLE 5] 1 g of activated carbon carrying 0.1 wt% of palladium was added to and immersed in a solution in which 0.01 g of isooctane was dissolved in 5 ml of ether, then the material was dried at 100°C for 30 minutes in a calcining oven and made a powder in a mortar, and then, in a glow box through which nitrogen gas was flowed, the material was added to and dispersed by stirring in 140 ml of a Sumitomo 3M Company Florinate FC-43 solution in which 50 g of the Du Pont Corporation's Teflon AF No. 1600 was dissolved. Next, this solution was coated on the structural unit used in Example 4 to produce a cast film and constitute a protective sealing layer (film thickness 0.2 millimetres).

[0091] [EXAMPLE 6] 0.5 g of a powder of cobalt monoxide (II) was dispersed by the same procedure as in Example 4 in a solution in which 50 g of the Du Pont Corporation's Teflon AF No. 1600 was dissolved in 100 ml of Florinate FC-43 (tradename; manufactured by Sumitomo 3M), and the resulting solution was coated on the structural unit used in Example 4 to produce a cast film and constitute a protective sealing layer (film thickness 0.5 millimetres).

[0092] [EXAMPLE 7] 0.1 g of vanadium oxalate was dissolved in 10 ml of distilled water, 10 g of activated alumina (tradename: Wako Gel; manufactured by Wako Junyaku) was added, and the material was stirred, dried solid in an evaporation dish and then put in an electric oven and heated for 2 hours at 600°C. The yellow powder which was produced was added to and mixed with paraffin (m.p. = 42-44°C) which had been heated to 50°C in a glow box through which nitrogen gas was flowed. The resulting solution was coated on the structural unit used in Example 4 and left to cool, so producing a thick film and constituting a protective sealing layer (film thickness about 1 millimetre).

[0093] [COMPARISON EXAMPLE 3] A solution in which 50 g of tetrafluorethylene and perfluoro-2,2-dimethyl-1,3-dioxole (tradename: Teflon AF No 1600; manufactured by Du Pont) was dissolved in 100 ml of the Sumitomo 3M Company's Florinate FC-43 was put into a glow box through which nitrogen gas was flowed, and this solution was coated on the structural unit

used in Example 4 to produce a cast film and constitute a protective sealing layer (film thickness 10 microns).

[0094] [COMPARISON EXAMPLE 4] Paraffin (m.p. = 42-44°C) heated to 50°C was coated on the structural unit used in Example 4 and left to cool in a glow box through which nitrogen gas was flowed, so producing a cast film and constituting a protective sealing layer (film thickness about 1 millimetre). With initial luminance at 100 cd/m², each of the organic EL elements of Examples 4-7 and Comparison Examples 3-4 was driven, in a glow box through which nitrogen gas was flowed, by constant-current continuous drive and by irregular drive in each month.

Key to table text page 16 (422)

- 1 Continuous drive
- 2 Half-life
- 4 Breakdown life
- 4 Irregular drive in each month (shelf life)
- 5 Example
- 6 Comparison Example
- 7 hours
- 8 ≥20000 hours
- 9 ≥10000 hours
- 10 ≥2000 hours
- 11 ≥1000 hours
- 12 No change after 12 months
- 13 Occurrence of dark spots after 1 month

...

Thus, rather than simply providing a protective sealing layer, better effects in respect of the half-life, breakdown life and storage life are had when a dehydrating agent is included in this layer.

[0095] [EXAMPLE 8]

Fabrication of organic EL element structural unit

Ultrasonic cleaning of a glass substrate (manufactured by the Matsuzaki Shinku Company) with a transparent electrode produced by forming a 1000 Å ITO (indium tin oxide) film on substrate glass was effected in acetone, and then boiling treatment in ethanol was effected. Further, treatment with a plasma possessing an air composition was effected. The glass substrate with a transparent electrode which had been given the above surface treatment was set in a vacuum unit and, at a vacuum of 5×10^{-6} torr, N,N'-diphenyl-N,N'-(3-methylphenyl)-1,1'-diamine (referred to below as TPD) was vapour-deposited to 200 Å, then a portion (graded structure portion) possessing a concentration gradient in which TPD and 8-oxyquinoline aluminium metal complex (referred to below as Alq³) components varied continuously was formed to 100 Å, and then Alq³ was vapour-deposited to 200 Å. Further, magnesium (Mg) and silver (Ag) were co-deposited, at an atomic ratio of 10:1, to 200 nm by vapour deposition, so producing an organic EL element structural unit.

[0096] Formation of protective layer

Next, Teflon AF No. 1600 manufactured by the Du Pont Corporation and magnesium powder were dispersed, in proportions to give a weight ratio of 100:1, in Florinate FC 72 manufactured by the Sumitomo 3M Company, and a protective layer was formed by using a dripping pipette to gently coat this dispersion on the structural unit which had been produced, waiting until it dried, and repeating the same operation several times. All the above operations were performed in a nitrogen atmosphere. Since an organic EL element thus produced is a completely solid element, it is easy to handle and there are no worries about leakage of liquid. When this element was left at room temperature in air and direct-current voltage was imposed on it, half a year later light was emitted uniformly, and there was no occurrence of defects in the element.

[0097] [COMPARISON EXAMPLE 5] An element was produced by procedure which was exactly the same except that magnesium powder was not added to the protective layer of the element of Example 8. When the resulting element, having been left to stand in air, was caused to emit light, a great number of macroscopically discernible large black defects were produced on the element's surface after 1 month.

[0098] [EXAMPLE 9] An element was produced by procedure which was the same except that Molecular Sieve 4A (manufactured by the Hiroshima Wako Company) was used instead of the magnesium constituting the dehydrating agent in Example 8. The result of this was that, for a period of 4 months, there was no occurrence of defects in the element.

[0099] [EXAMPLE 10] An element was produced by procedure which was the same except that anhydrous magnesium sulfide (manufactured by the Hiroshima Wako Company) was used instead of the magnesium constituting the dehydrating agent in Example 8. The result of this was that, for a period of 3 months, there was no occurrence of defects in the element.

Dehydrating agent	Performance	
Mg	6 months no defects	Example 8
Molecular Sieve 4A	4 months no defects	Example 9
Anhydrous Mg SO ₄	3 months no defects	Example 10
None	Occurrence of defects at 1 month	Comparison Example 5

For the performance, the state of light emission surfaces on imposition of a direct-current voltage of 10V was examined.

[0100] [EXAMPLE 11] Fabrication of organic EL element structural unit

The transparent support substrate employed was one in which ITO was formed as a film to a thickness of 10 nm by vapour deposition procedure on a 25 mm x 75 mm x 1.1 mm glass substrate. After 5 minutes washing of this transparent support substrate in isopropyl alcohol, 5 minutes ultrasonic cleaning was effected in pure water, and, further, UV ozone cleaning was effected for 5 minutes. A unit manufactured by

Samc International Laboratories was used for this UV ozone cleaning. This transparent support substrate was fixed to the substrate holder of a commercially available vapour deposition unit (manufactured by the Nihon Shinku Gijutsu Company), 200 mg of N,N'-bis(3-methylphenyl)-N,N'-diphenyl[1,1'-biphenyl]-4,4'-diamine (TPD) was put into a resistance heating boat made of molybdenum, 200 mg of 4,4'-bis(2,2'-diphenylvinyl)biphenyl (DPVBi) was put into another resistance heating boat made of molybdenum, and the pressure of the vacuum chamber was reduced to 1×10^{-4} Pa. After that, TPD was vapour-deposited on the transparent support substrate at a vapour deposition rate of 0.1 - 0.3 nm/second to form a positive hole injection layer with a film thickness of 60 nm. The substrate temperature at this time was room temperature. Without the resulting element being taken from the vacuum chamber, DPVBi from the other boat was vapour-deposited to 40 nm as a light-emitting layer on the positive hole injection. The vapour deposition conditions were that the boat temperature was 240°C, the vapour deposition rate was 0.1 - 0.3 nm/second, and the substrate temperature was room temperature. The resulting element was taken out from the vacuum chamber, a mask made of stainless steel was set on the light-emitting layer, and the element was fixed to the substrate holder again. Next, 200 mg of tris(8-quinolinol) aluminium (Alq^3) was put into a molybdenum boat and was set in the vacuum chamber. Further, 1 g of magnesium ribbon was put into a resistance heating boat made of molybdenum, 500 mg of silver wire was put separately into a basket made of tungsten, and vapour deposition was effected. After that, the pressure of the vacuum chamber was reduced to 1×10^{-4} Pa, the boat containing Alq^3 was heated to 230°C, and Alq^3 was vapour-deposited to 20 nm at a vapour deposition rate of 0.01 - 0.03 nm/second. At the same time, a commencement was made to vapour deposition of silver at a vapour deposition rate of 0.01 nm/second by resistance heating procedure and to vapour deposition of magnesium from the other molybdenum boat at a vapour deposition rate of 1.4 nm/second. In these conditions, a magnesium and silver metal mixture electrode was vapour-deposited and built up to a thickness of 500 nm on the light-emitting layer, constituting a facing electrode. The resulting element structural unit was aged by the imposition,

in dry nitrogen and for 5 seconds each time, of voltages in the intervals from 0V to 10V and from 0V to -10V to 0.5V.

[0101] Formation of sealing layer

Next, silica glass with an average particle diameter of 1 μm (manufactured by the Shokubai Kasei Company) was mixed, in the proportion of 70 wt%, in a visible light curing type adhesive (tradename: Arontite [Tr. note: Transliteration] VL; manufactured by the Toa Gosei Kagaku Kogyo Company) to constitute a sealing layer. This sealing layer was dripped in a manner such as to cover the electrode and organic multilayer portions of the abovedescribed element structural unit, and was cured by sunlight, so resulting in the formation of a sealing layer 1 mm thick.

[0102] [COMPARISON EXAMPLE 6] An element structural unit was fabricated to the same structure and by the same work procedure as in Example 11 and, using the material with the tradename Arontite VL manufactured by Toa Gosei Kagaku Kogyo, a sealing layer was formed on the structural unit in the same conditions as in Example 11. When 50 sealed elements each of Example 11 and Comparison Example 6 were fabricated, the numbers of elements with which light emission capacity completely disappeared because of mechanical breakdown or shorting due to sealing were 5 in Example 11 and 40 in Comparison Example 6. Further, 10 each of the sealed elements of Example 11 and Comparison Example 6 were set in a durability test unit (SH-220 manufactured by the Tabae Esbeck (Tr. note: Transliteration) Company), and were subjected to a heat cycle durability test consisting of 10 times repetition of heat cycles in which the temperature was varied in a manner making $25^{\circ}\text{C} \rightarrow 60^{\circ}\text{C}$ 30 minutes and making $60^{\circ}\text{C} \rightarrow 25^{\circ}\text{C}$ 30 minutes. The result of this was that the numbers of elements that became elements possessing no capacity at all to emit light were 2 in Example 11 and 7 in Comparison Example 6. It was thus clear that Example 11 improved the yield at the time of fabrication and improved the heat cycle durability relative to Comparison Example 6.

[0103] [EXAMPLE 12] Fabrication of organic EL element structural unit

Ultrasonic cleaning of a glass substrate with a transparent electrode (manufactured by the Diomatick (Tr. note: Transliteration) Company) in which a 1000 Å ITO (indium oxide - tin oxide) film was formed on substrate glass was effected in acetone, and then cleaning was effected in a UV cleaning unit (UV-300 manufactured by Samco International Laboratories). The glass substrate with a transparent electrode which had been given the above surface treatment was set in a vacuum unit, and, with the degree of vacuum at 5×10^{-5} torr, N,N'-(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine (TPD) was vapour-deposited to 600 Å, and then the 8-hydroxy-quinolinol aluminium complex Alq³ was vapour-deposited to 500 Å. Further, magnesium (Mg) and silver (Ag) were co-deposited, at an atomic ratio of 10:1, to 2000 Å by vapour deposition, so producing an organic EL element structural unit.

[0104] Formation of laminate

In a vacuum ($\leq 10^{-4}$ torr) the above element structural unit was covered with Saran Wrap (oxygen permeability coefficient of Saran Wrap: 5.3×10^{-13} cc.cm/cm².s. (cmHg)), and its edge portions were hot-pressed (180°C, 10 seconds). The element thus fabricated was subjected to constant-current drive at an initial luminance of 100 cd/m² in the same evaluation conditions as described earlier.

[0105] [COMPARISON EXAMPLE 7] A structural unit as used in Example 12, but without the provision of a laminate thereon was subjected to continuous drive, in the evaluation conditions noted below, by constant current, with the initial luminance at 100 cd/m². After the two units had been continuously driven for 500 hours, the light emission area in the element was 3.95 cm² in the case of Example 12, whereas it was 2 cm² in the case of Comparison Example 7. The evaluation conditions were that drive (in a glass case) was effected in 25°C dry air (1:4 gas mixture of 99.99% pure oxygen and nitrogen). This result showed that effecting sealing as in

Example 12 has the effect of suppressing the occurrence of n n-light-emitting regions.

[0106]

[Advantages of the invention] As described above, the 1st-3rd and 5th inventions in the present invention make it possible to prevent deterioration of light emission characteristics caused by oxygen or moisture and to maintain stable light emission characteristics over a long period, and so make it possible to provide long-life organic EL elements. Also, the 4th invention in the present invention makes it possible to prevent mechanical degradation of elements by heat cycles, maintain stable light emission characteristics over a long period and provide long-life organic EL elements. Further, suitably combining the 1st-5th inventions makes it possible to prevent deterioration of elements due to oxygen, moisture and heat cycles, and so makes it possible to provide organic EL elements whose product quality is still more superior.

[BRIEF DESCRIPTION OF THE DRAWINGS]

[Fig. 1] is a cross-section which schematically shows a specific example of a 1st invention in the present invention.
[Fig. 2] is a cross section which schematically shows a specific example of a 2nd invention in the present invention.
[Fig. 3] is a cross-section which schematically shows a specific example of a 3rd invention in the present invention.
[Fig. 4] is a cross-section which schematically shows a specific example of a 4th invention in the present invention.
[Fig. 5] is a cross-section which schematically shows a specific example of a 5th invention in the present invention.
[Fig. 6] is a cross-section which schematically shows another specific example of the 5th invention in the present invention.
[Fig. 7] is a cross-section which schematically shows another specific example of the 5th invention in the present invention.

[Explanation of symbols]

1 ... Structural unit
10 ... Organic EL element

- 11 ... Substrate
- 12 ... An de
- 13 ... Cathode
- 14 ... Organic light-emitting material
- 2 ... Laminate
- 2' ... Protective sealing layer
- 21 ... Organic layer whose oxygen permeability coefficient is
 $\leq 1 \times 10^{-12}$ cc.cm/cm².s (cmHg)
- 3 ... Protective layer
- 4 ... Sealing layer
- 41 ... Oxygen absorption layer
- 42 ... Oxygen barrier layer
- 43 ... Photo-or thermosetting resin layer
- 44 ... Inorganic composition
- 5 ... Frame (made of glass or resin)
- 6 ... Adhesive layer
- 7 ... Sealing substrate
- 8 ... Solid case

Key to drawings

Fig. 1 (text sheet 18)

- 1: Structural unit
- 2: Laminate
- 3: Protective layer
- 4: Sealing Layer
- 5: Frame
- 10: Organic El element
- 11: Substrate
- 12: Anode
- 13: Cathode
- 14: Organic light-emitting material
- 41: Oxygen absorption layer
- 42: Oxygen barrier layer

Fig. 2 (text sheet 18)

- 2': Protective sealing layer
(Layer containing material which effects oxygen adsorption etc.)
- 6: Adhesive layer
- 12: Anode
- 13: Cathode

Fig. 3 (text sheet 19)

- 31: Dehydrating agent

Fig. 4 (text sheet 19)

- 43: Photo - or thermosetting resin layer
- 44: Inorganic composition

Fig. 5 (text sheet 19)

- 21: Organic layer whose oxygen permeability coefficient is $\leq 1 \times 10^{-12}$ cc.cm/cm².S (cmHg)

Fig. 6 (text sheet 19)

- 7: Sealing substrate

Fig. 7 (text sheet 19)

- 8: S lid case

【0104】積層体の形成

この素子の構造体を真空中 (10^{-4} torr 以下) にて、この素子の構造体上に旭化成社製、商品名：サランラップ (サランラップの酸素透過係数は 5.3×10^{-11} cc・cm/cm²・s・(cmHg)) をかぶせ、素子の構造体の端の部分熱プレス (180℃、10秒) した。以上のように作製した素子を下記の評価条件下にて初期輝度 100 cd/m^2 にて定電流駆動した。

【0105】【比較例7】実施例12で用いた構造体をその上に積層体を形成することなく、初期輝度 100 cd/m^2 にて定電流駆動で下記の評価条件下にて連続駆動した。両者500時間連続駆動後、素子内の発光面積は実施例12の場合 3.95 cm^2 に対し、比較例7の場合 2 cm^2 であった。評価条件は25℃乾燥空気 (純度99.99%以上の酸素とチッ素の1:4の混合気体) 中 (ガラスケース内) で駆動した。その結果、実施例12に示すように、封止することで無発光領域の発生を抑制する効果がみられた。

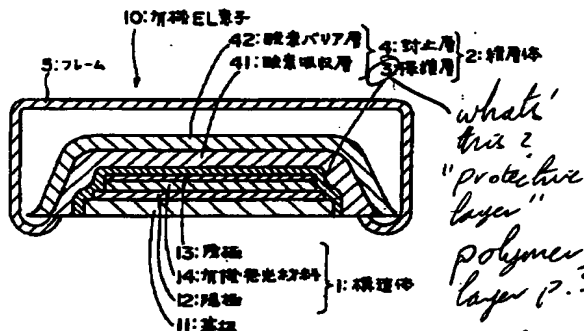
【0106】

【発明の効果】以上説明したように、本発明の第一〜第三、及び第五の発明によれば酸素や水分による発光特性の劣化を防止して、長期に亘って安定な発光特性を維持することができ、長寿命の有機EL素子を提供することができる。また、本発明の第四の発明によれば、温度サイクルによる素子の機械的劣化を防止して長期に亘って安定な発光特性を維持することができ長寿命の有機EL素子を提供することができる。さらに、第一〜第五の発明を適宜組み合わせることによって酸素、水分、温度サイクル等による素子の劣化を防止して、さらに品質の優れた長寿命の有機EL素子を提供することができる。

【図面の簡単な説明】

【図1】本発明の、第一の発明の具体例を模式的に示す断面図である。

【図1】



42 = protective (dielectric) layer
41 = oxygen absorbing layer.

【図2】本発明の、第二の発明の具体例を模式的に示す断面図である。

【図3】本発明の、第三の発明の具体例を模式的に示す断面図である。

【図4】本発明の、第四の発明の具体例を模式的に示す断面図である。

【図5】本発明の、第五の発明の具体例を模式的に示す断面図である。

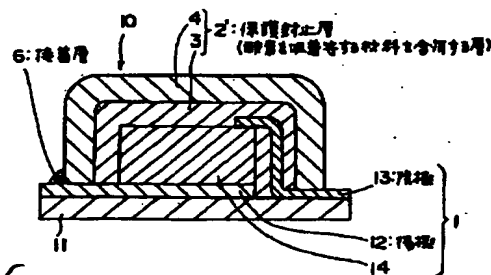
【図6】本発明の、第五の発明の他の具体例を模式的に示す断面図である。

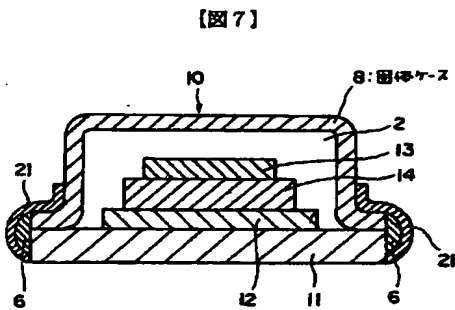
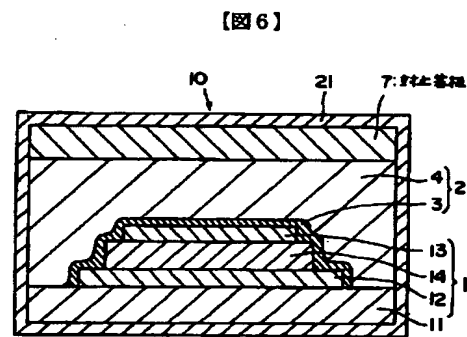
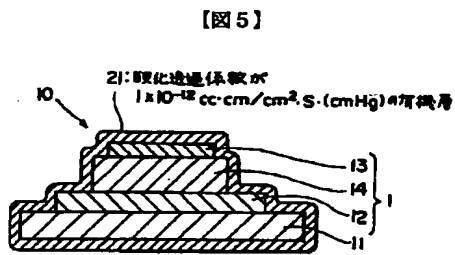
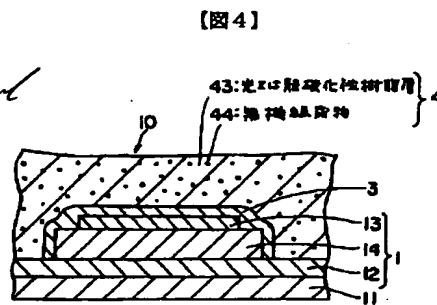
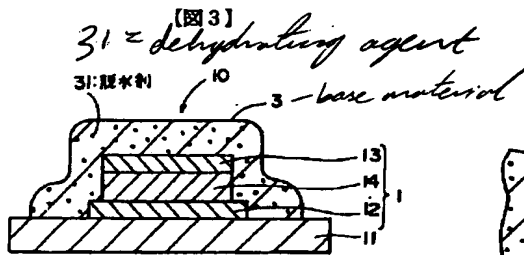
【図7】本発明の、第五の発明の他の具体例を模式的に示す断面図である。

【符号の説明】

- 1…構造体
- 10…有機EL素子
- 11…基板
- 12…陽極
- 13…陰極
- 14…有機発光材料
- 2…積層体
- 2'…保護封止層
- 21…酸化透過係数が 1×10^{-12} cc・cm/cm²・s・(cmHg) の有機層
- 3…保護層
- 31…脱水剤
- 4…封止剤
- 41…酸素吸収層
- 42…酸素バリア層
- 43…光または熱硬化性樹脂層
- 44…無機組成物
- 5…フレーム (ガラスまたは樹脂製)
- 6…接着層
- 7…封止基板
- 8…固体ケース

【図2】





フロントページの続き

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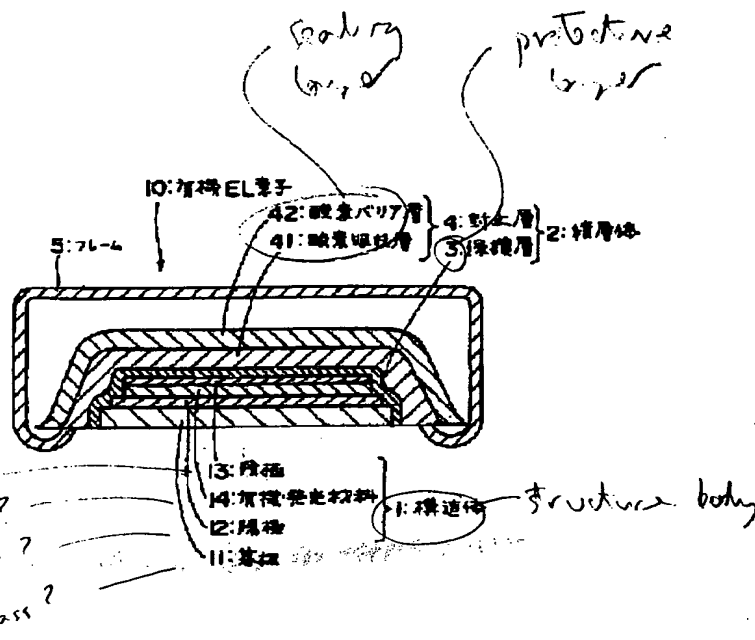
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INVENTOR : KAWAMURA HISAYUKI;

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ABSTRACT : **PURPOSE:** To prevent the degradation of a light emitting characteristic caused by oxygen or moisture, and maintain a stable light emitting characteristic over a long period of time by arranging a layer of double layers composed of an oxygen barrier layer and an oxygen absorbing layer as a sealing layer of a layered body.

CONSTITUTION: A sealing layer 4 is arranged outside of a structure body 1 as a layered body 2 through a protective layer 3. This sealing layer 4 is composed of one or more sets of double layers by forming an oxygen absorbing layer 41 and an oxygen barrier layer 42 as a single set. An organic compound, an oxygen absorbing compound, a fluorine compound, metallic fine powder and the like having small ionization potential are used as a material used in the oxygen absorbing layer 41. Metallic oxide, nitride, fluoride and the like used as the protective layer 3 are used as the oxygen barrier layer 42.

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